

## C K-edge X-ray Absorption Spectroscopy of Sodium Inserted Hard Carbon

Ami Soyama<sup>1</sup>, Daisuke Shibata<sup>2</sup>, Chengchao Zhong<sup>1</sup>, Keiji Shimoda<sup>3</sup>,  
Ken-ichi Okazaki<sup>1,2</sup> and Yuki Orikasa<sup>1</sup>

- 1) Department of Applied Chemistry, Graduate School of Life Sciences, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu 525-8577, Japan
- 2) Research Organization of Science & Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, 525-8577, Japan
- 3) Ritsumeikan Global Innovation Research Organization, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, 525-8577, Japan

Sodium-ion batteries are expected to be commercialized as low-cost rechargeable batteries. Although graphite cannot be used as the anode active material, hard carbon has been reported to undergo an electrochemical sodium ion insertion/extraction reaction. The analysis of sodium-ion insertion to hard carbon is important to develop the high-performance anode materials. To the best of our knowledge, C K-edge X-ray absorption near edge structure (XANES) of hard carbon with sodium ion insertion have not been reported. This is partly due to the presence of carbon species in the surface film components formed during the electrochemical reaction, which makes the spectra complicated to analyze. One chemical method for synthesizing alkali metal-graphite intercalation compounds (AM-GICs) is the solution method, in which alkali metals react with graphite in organic solvents. However, because organic solvents are highly polar, the solvent molecules are also co-intercalated [1]. It has been shown that AM-GICs can be synthesized by using the optimized combination of alkali metals and solvents [1]. In this study, we use this synthetic method to chemical sodium insertion into hard carbon without the influence of a surface film. C K-edge XANES of the obtained samples is discussed.

Synthesis of sodium intercalated hard carbon was performed in a glove box under Ar atmosphere. Sodium metal (Sigma-Aldrich) and hard carbon (MTI corporation) were weighed in a molar ratio of 3:1. Sodium metal and 1 M biphenyl (Fujifilm Wako Pure Chemicals Corporation) were dissolved in 100 mL of dimethyl ether (DME, Kishida Chemical Corporation). Hard carbon was then added and stirred for approximately 2 days. The powder was removed by filtration and washed with DME solution. C K-edge XANES measurements of the synthesized powder and pristine hard carbon were performed at the beamline of the SR Center, Ritsumeikan University in a total electron yield mode. The synthesized samples were transported to the sample chamber without air exposure.

C K-edge XANES of the pristine and sodium inserted hard carbons are shown in Fig. 1. The spectrum of the sodium inserted hard carbon exhibits sharp peaks at 285, 289, and 290 eV and broad

structures at 297 and 301 eV. On the other hand, the pristine hard carbon shows the characteristic peak at 285 eV and a broad structure at higher energy. The peak at 285 eV observed in both samples is attributed to the transition from C1s to the  $\pi^*$  (C = C). For the other peaks, the peaks do not coincide before and after sodium insertion. In the C K-edge electron energy loss spectroscopy of LiC<sub>6</sub>, a graphite interlayer compound, the peak is observed around 301 eV, which is not observed in graphite [2]. Therefore, the peak at 301 eV is considered to be originated from the inserted alkali metal ions. The hard carbon synthesized in this study after sodium insertion also shows a peak around 301 eV, which is not observed in the pristine hard carbon. This suggests that the hard carbon after chemical insertion reaction contains sodium ion in the structure.

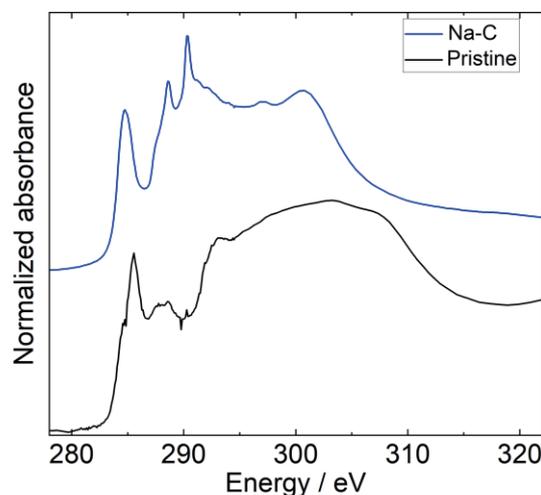


Fig. 1 C K-edge XANES of the pristine and sodium inserted hard carbons.

### References

- [1] Y. Mizutani, T. Abe, M. Inaba, and Z. Ogumi, *Synthetic Metals*, **2001**, 125, 153.
- [2] A. Hightower, C. C. Ahn, and B. Fultz, *Appl. Phys. Lett.*, **2000**, 77, 238.